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TITLE		
ETHYLENE OXIDE FUEL, DIAPHRAGM MATERIAL "CALIFILM", UNPLASTICIZED KEL-F, FOR USE IN XQ-5		
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MSD-3066	11-20-56	XQ-5
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LOCKHEED AIRCRAFT CORPORATION

MSD-3066

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ENGINEERING TEST DEPARTMENT (72-30) — DATED Nov[redacted], 1956

Chemical-Metallurgical Section, Group 41 — REF: SN/9?2

SUBMITTED UNDER (15) AF 33(600)-27591 — MODEL XQ-5

REQUESTED BY F. H. Turner (77-20) — CHARGE 3-1321-1362-07

PREPARED BY (10) A. T. Caufield — GROUP APPROVAL C. W. Mell

(6) [redacted]: ETHYLENE OXIDE FUEL, DIAPHRAGM MATERIAL "CALIFILM", UNPLASTICIZED KEL-F, FOR USE IN XQ-5

OBJECT:

(12) 11p.

The purpose of these tests was to determine the effect of ethylene oxide containing 1/4 of 1% carbon disulphide on a sheet of KEL-F material containing no plasticizer. A diaphragm material resistant to ethylene oxide is desired for use in fuel cells which could be operated in the XQ-5 missile.

INTRODUCTION:

Previous reports MSD-1817 and MSD-3005 covered tests of a plasticized KEL-F (LP-20) material in contact with liquid ethylene oxide which contained 1/4 of 1% of carbon disulphide. After an exposure time of one week at 200°F, the material lost 19.4% of its weight. Tests run at 150°F showed the weight loss to be 19.28%. The plasticizer appeared to behave as a catalyst in promoting polymerization of the ethylene oxide, and a polymerization residue of 0.57% based on the weight of ethylene oxide was obtained. The material was judged unsuitable and it was the proposed to conduct additional tests on a KEL-F material containing no plasticizer. This material is designated "Califilm" and is supplied by the Shamban Engineering Co., 11617 W. Jefferson Blvd., Culver City, California. This report gives the results of tests conducted on the untreated samples and on material exposed to liquid ethylene oxide containing 1/4 of 1% carbon disulphide for one week at 150°F.

CONCLUSIONS:

1. The material is not uniform in thickness. While supposed to have a nominal thickness of 0.010", the actual thickness varied from 0.00825" to 0.014". It is believed that this wide variation would make this particular sheet material unsuitable.

2. Calender markings on the sheet are undesirable. They cause marked anisotropic behavior.

3. The sheet material exhibits greatest strength and percent elongation in a direction parallel to the calender markings.

(210 120)

CONCLUSIONS: (Continued)

4. Due to the calender markings and variations in thickness, there is wide variation in tensile and elongation values obtained from different specimens cut in the same direction. The greatest variation occurs in specimens where the markings are normal to the long axis of the specimen.

5. The KEL-F sheet, unexposed to ethylene oxide, had an average tensile strength in a direction parallel to the markings of 5833 psi and the percent elongation at failure was 143%. For specimens with markings normal to the long axis, the corresponding figures are 5400 psi and 110% respectively.

6. Specimens exposed to liquid ethylene oxide under the test conditions, and then allowed to stand at room temperature for 140 hours to dissipate any absorbed ethylene oxide, showed increases in weight. This weight increase averaged 1.16% for samples 0.0095" in thickness, and 1.43% for samples 0.0125" in thickness. Average weight increase for all samples was 1.30%. This increase appears to be permanent and is probably due to chemical reaction rather than physical absorption.

7. Exposure to ethylene oxide for one week at 150°F resulted in lowering the tensile strength to 2885 psi, a reduction of about 48.5%.

8. Exposure to ethylene oxide increased the percent elongation at failure from 122% for untreated material to 288% for exposed material.

9. While no tensile measurements were made on Califilm immediately after removal from the liquid ethylene oxide, the material was very much more pliant and yielding than after all the ethylene oxide had diffused out of it. It is therefore to be expected that if such measurements had been made, they would have shown considerably lower tensile values and higher percent elongation at failure in the ethylene oxide saturated condition.

10. If physical properties are to be used in design, it is very important that the marked difference in behavior between material in saturated and ethylene oxide free condition be taken into account.

11. If the dimensional difficulties of the present sheet material can be overcome, it might be advisable to thoroughly investigate the physical properties in the saturated state, since the material will be required to perform in that condition.

12. Polymerization residue obtained from the exposure test was 0.0375% based on the weight of ethylene oxide used. This compares with 0.57% for a similar test with a plasticized KEL-F reported in MSD-3005. This low value for polymerization residue is believed to rate the Califilm as excellent in this respect. It further

CONCLUSIONS: (Continued)

12. - continued:

indicates its marked superiority over the plasticized KEL-F.

13. Califilm exposed to ethylene oxide picks up 3.37% of its weight. About 2% of this is merely absorbed as ethylene oxide and is released slowly when the samples are exposed in air at room temperature. The remainder is held by the material, probably as a chemical addition.

14. Comparison of Califilm with the plasticized KEL-F (LP-20, previously investigated in MSD Report #3005) shows that in the untreated state the Califilm has approximately twice the tensile strength of the plasticized material. While both materials suffer considerable loss in strength on exposure to liquid ethylene oxide, the Califilm still has a 36% higher tensile strength after one week's exposure at 150°F.

PROCEDURE:

Test specimens were prepared of the usual "dumbbell" type used for tensile determinations. These, in dimensions, conformed to ASTM D638-52T, Type I. Twelve samples were prepared for tensile tests of unexposed material. Six of these were cut so that the calender markings were parallel to the long axis of the specimens, and six were cut so that the markings were at right angles to the long axis.

Four samples were prepared for use in the exposure test, two with calender markings parallel to the long axis and two at right angles to it. Since any conventional marking would probably be removed by the ethylene oxide (and it was desirable not to mark the exposure specimens mechanically), specimens were cut successively shorter in length and identified by this means.

Exposure samples were weighed before being placed in the pressure vessel. After the test period, the specimens were removed and weighed at intervals up to 141 hours.

The pressure vessel used has been described previously (MSD Report #3005). The specimens to be exposed were placed in the vessel which was then connected to the ethylene oxide storage tank by means of a piece of 3/16" stainless steel tubing. Liquid ethylene oxide was then run into the open vessel to a point somewhat above a predetermined level. The liquid was allowed to boil down to this level and a quantity of carbon disulphide, calculated to give 1/4 of 1% by weight of the ethylene oxide, then added. The mixture was then stirred with a glass rod and the lid screwed on and tightened securely. The system was checked for leaks and the assembly placed in a thermostatically controlled oven at 150°F. It was maintained at this temperature for one week.

The pressure vessel was then removed from the ofen and allowed to cool to room temperature. The ethylene oxide was discharged into a weighed 50 ml.

PROCEDURE: (Continued)

beaker in several steps. The oxide was evaporated on the hot plate at 220°F and the polymerization residue obtained by difference. The pressure vessel was then opened and the samples removed for the weight determinations.

Tensile tests were run on a Baldwin-Emery SR-4 testing machine.

RESULTS:

Table 1

Tensile Tests on Untreated Califilm

Calender Marks - Lengthwise

SAMPLE NO.	THICKNESS (Inches)	TENSILE STRENGTH (Psi)	% ELONGATION AT FAILURE
1	0.0136	6034	168.8
2	0.0120	6122	93.8
5	0.0130	5420	187.5
6	0.0140	5380	93.9
7	0.0120	5610	200.00
8	0.0125	6430	112.5
Average	0.0129	5833	142.8

Calender Marks - Transverse

SAMPLE NO.	THICKNESS (Inches)	TENSILE STRENGTH (Psi)	% ELONGATION AT FAILURE
3	0.0083	2863	37.5
4	0.0090	7289	106.3
9	0.0085	7300	100.0
10	0.0100	4150	137.5
11	0.0090	5345	162.5
12	0.0090	5450	118.8
Average	0.0091	5400	110.4

Figure 1 shows the appearance of the calendering marks. The material seems to be piled up at the site of the markings in the form of a series of small V's, the bottom of the V pointing in the direction of rolling.

Figure 2 shows an enlarged photomicrograph showing portions of two such calendor markings.

Figure 3 shows one such calender marking as observed under high magnification on the microscope. The variation in thickness is clearly evident in the marking.

RESULTS: (Continued)

Table 2

Measurements on the Test Samples
Before Exposure to Ethylene Oxide

	SAMPLE #1	SAMPLE #2	SAMPLE #3	SAMPLE #4
Length	8.47	8.27	8.00	7.74
Width	0.4990	0.5000	0.5070	0.4910
Thickness	0.0115	0.0130	0.0090	0.0090
Weight	2.2445	2.3610	1.6111	1.5555
Calender marks	Lengthwise	Lengthwise	Transverse	Transverse

Table 3

Weights of Specimens at Various Times
After Removal from the Ethylene Oxide

HOURS AFTER SAMPLE WAS REMOVED	SAMPLE #1	SAMPLE #2	SAMPLE #3	SAMPLE #4
0	2.3270	2.4475	1.6620	1.6035
2.25	2.3042	2.4265	1.6499	1.5924
68.50	2.2796	2.4010	1.6329	1.5762
71.50	2.2795	2.4008	1.6330	1.5761
140.75	2.2756	2.3955	1.6301	1.5732

Table 4 shows the weights of samples immediately after removal from the liquid ethylene oxide and when they were essentially in the saturated condition. The samples were completely surface dry and exhibited no visual difference from untreated material. Physically, however, there was a marked difference. The material was much more limber and less springy than the untreated Califilm. After standing for 140 hours and losing the entrapped ethylene oxide, the specimens seemed to regain much of their original properties.

Table 4

Weights of Samples Before and After Removal from Ethylene Oxide

SAMPLE #	ORIGINAL WEIGHT	WEIGHT IMMEDIATELY AFTER REMOVAL FROM ETHYLENE OXIDE	WEIGHT INCREASE	% WEIGHT INCREASE
1	2.2445	2.3270	0.0825	3.69
2	2.3610	2.4475	0.0865	3.53
3	1.6111	1.6620	0.0509	3.16
4	1.5555	1.6035	0.0480	3.09

Average % weight increase (saturated condition) - 3.37

RESULTS: (Continued)

Table 5 gives comparable figures for the samples after they were allowed to stand for 140 hours to lose their residual ethylene oxide. It is unusual that, as shown in both Tables 4 and 5, the higher percent weight increase in both the saturated and dried condition occurred in the thicker specimens. No adequate explanation is, at present, available to account for this phenomenon. Possible future work on thicker material may confirm these observations and throw some light on this behavior. The actual processes, heat treatment, etc., used to produce the sheet, probably have an important bearing on its properties and behavior.

Table 5

SAMPLE #	ORIGINAL WEIGHT	WEIGHT AFTER 140 HOURS AT ROOM TEMPERATURE	WEIGHT INCREASE	% WEIGHT INCREASE
1	2.2445	2.2756	0.0311	1.39
2	2.3610	2.3955	0.0345	1.46
3	1.6111	1.6301	0.0190	1.18
4	1.5555	1.5732	0.0177	1.14

Average % weight increase (dry condition) - 1.30

Table 6

Tensile Tests on Exposed Califilm

Calender Marks - Lengthwise

SAMPLE NO.	THICKNESS (Inches)	TENSILE STRENGTH (Psi)	% ELONGATION AT FAILURE
1	0.012	3330	212.5
2	0.013	2440	325
Average	0.125	2885	268.8

Calender Marks - Transverse

SAMPLE NO.	THICKNESS (Inches)	TENSILE STRENGTH (Psi)	% ELONGATION AT FAILURE
3	0.0095	2570	262.5
4	0.0090	3200	331.8
Average	0.00925	2885	297.2

Table 6 gives results on exposed samples which were allowed to remain at room temperature for 140 hours before pulling in the tensile machine.

FURTHER WORK:

Since the material has good tensile strength and elongation properties and produces a low polymerization residue, it appears worthwhile to study it further.

Because exposure to ethylene oxide reduces the tensile strength markedly and because such strength is again further reduced when the material is in a saturated condition, a sheet having sufficient thickness would have to be chosen to allow for these reductions. While stress analysis is beyond the scope of this investigation, some effort should be made to determine just what tensile strength is required in the application. From this, with a proper factor of safety, the required thickness of material could be calculated. Because such data is not now available, only a general impression can be given. It is felt that 0.010" material is probably too thin to use.

Efforts should be made to obtain a material which is more uniform dimensionally; also, the material should be free of calender markings. The vendor should be questioned regarding these matters and actual processing methods. Such information might shed some light on the observed behavior of the material. If processing methods and limitations are known in detail, it might be conceivable that a material similar to that tested could be used if sufficient allowance were made for the variation inherent in the material.

In further test work where determination of weight change may not be necessary, tensile tests should be run on specimens in as close to saturated condition as possible, since this is the environment under which the diaphragm will be required to perform.

Information recently acquired from M. W. Kellogg Company, manufacturers of KEL-F, indicates that the Califilm tested was an extruded material. They advise that for a diaphragm material, much better results may be obtained by spraying a KEL-F dispersion onto a metal back-up sheet of the proper configuration. Any desired thickness may be built up. The coating after spraying is heated to 500°F to coalesce the individual particles and produce a continuous sheet free of pinholes and h... all the desirable properties of an extruded material. Thickness may be held to 0.001". This should produce a diaphragm with more uniform mechanical properties.

REFERENCES:

1. Engineering Test Request No. 0028 from F. H. Turner (77-20) dated 6/18/56, SN/922

2. IDC - OD/9116 from A. T. Caufield to J. Hunnell dated 8/6/56.

3. MSD Report No. 1817

4. MSD Report No. 3005

5. Discussions with F. H. Turner (77-20), B. Stankus (73-30) and J. Britten (73-30)

6. Interoffice Notebook Pages 197875-197882 inclusive

FIGURE 1

CALIFILM SHOWING CALENDERING MARKS

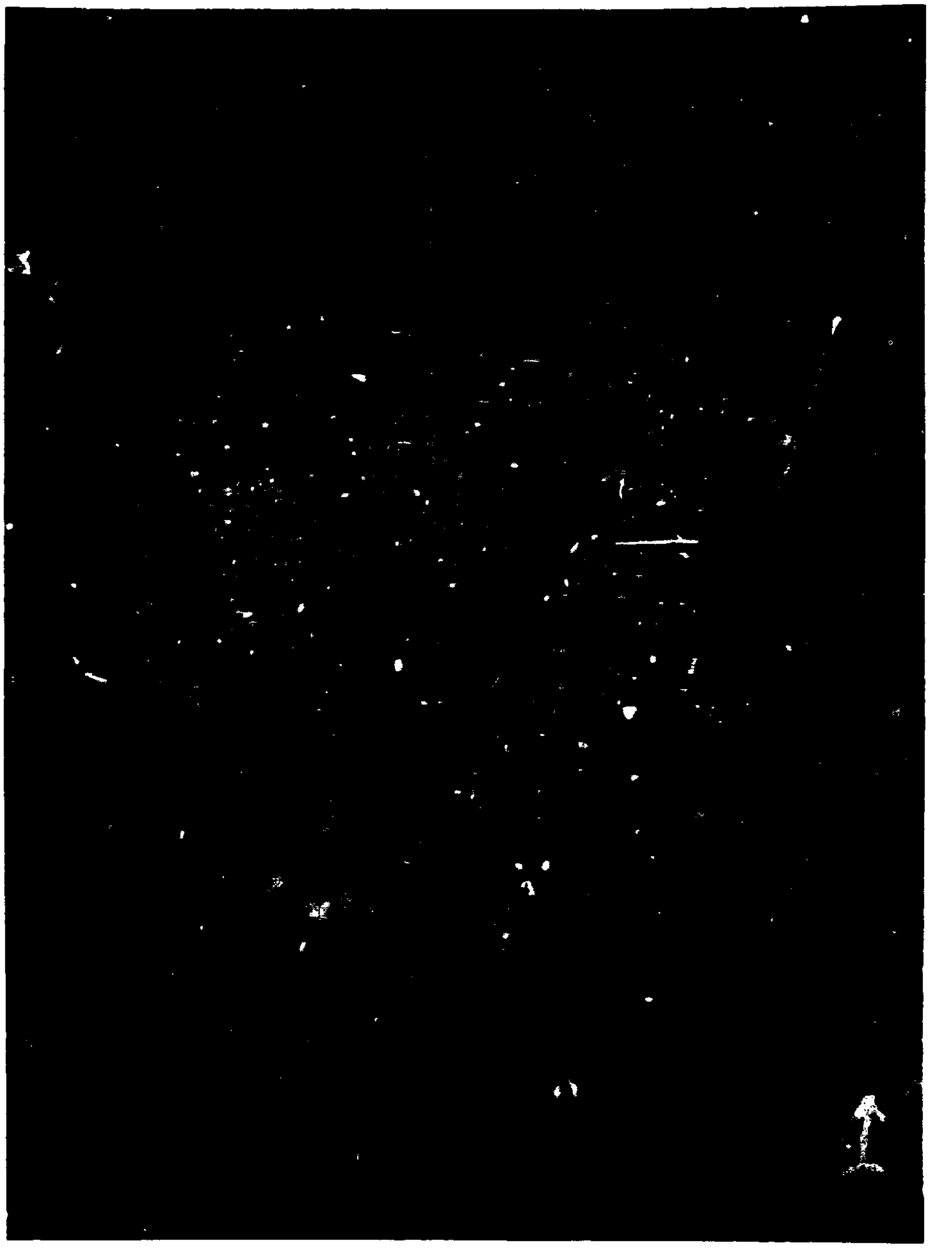

FIGURE 2

PHOTOMICROGRAPH OF CALIFILM SHOWING PORTIONS
OF TWO CALENDER MARKINGS

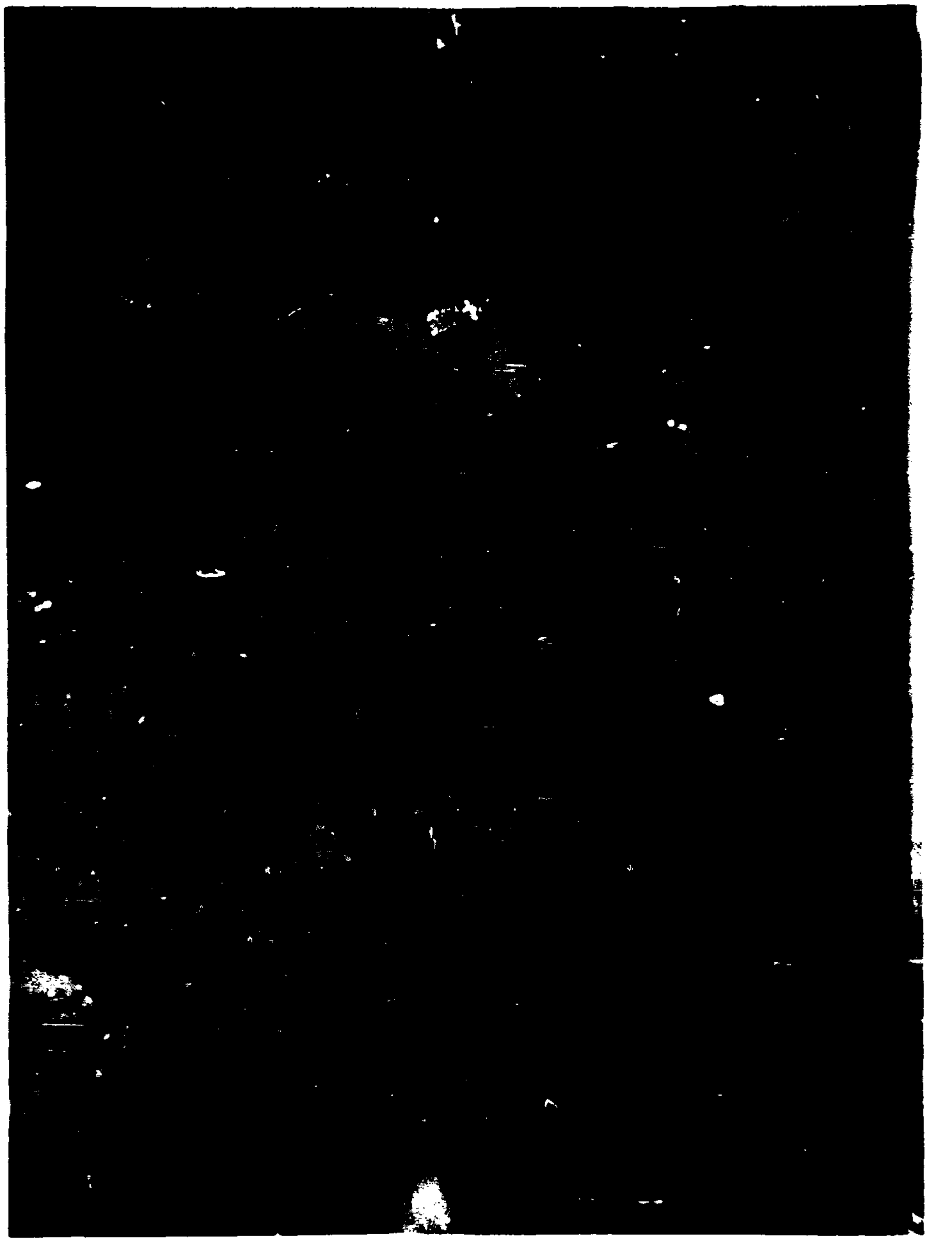

FIGURE 3

PHOTOMICROGRAPH OF CALIFILM SHOWING
ONE CALENDER MARKING
Variation in thickness is clearly evident.